METHOD FOR PRODUCING A PHOTOVOLTAIC DEVICE

The present invention relates to a method for producing a photovoltaic device comprising a photovoltaic cell including at least one film of a semiconductive metal oxide.

Semiconductive metal oxides such as oxides of titanium, zirconium, hafnium, strontium, zinc, indium, yttrium, lanthanum, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, show a crystalline phase exhibiting photocatalytic functionality, and can be use in a variety of applications. For example, Titania (TiO_2) has several crystalline phases such as anatase, rutile and brookite. Among these crystalline phases, the anatase one exhibits higher photocatalytic properties and photovoltaic effect and thus has attracted much attention in these fields.

Nanosized anatase titania film have been studied for applications such as solar cells, photocatalysts, antibacterial coating, electrochromic display, anti-reflecting coating and gas sensors. The photovoltaic devices fall within the general class referred to as dye-sensitized solar cells, as reported, e.g., by US 2003/0188776.

Presently, many applications would benefit from the availability of a photovoltaic cell or module, for example, the so-called "smart cards", i.e., electronic cards capable of storing information and used, e.g., for payphone telephony, digital mobile telephony, the credit and debit functions of financial institutions, retail loyalty schemes, corporate staff systems, subscription TV operations, mass transit ticketing schemes and the like.

Typically, these cards comprises an information module, which provides information (e.g., electronic data or an audiovisual response) to a user or to a card reader, and a photovoltaic cell that powers the information module. The information module and the photovoltaic cell are typically supported on a polymeric substrate.

Thin films based on nanoparticles of anatase titania show high photocatalytic activity depending on phase, crystal dimension and surface area, and porosity. As reported by Yoshinori Kotani et al. Journal of Sol-Gel

Science and Technology 19, 585-588, 2000, the sol-gel method is one of the most promising techniques to prepare thin films because it has a number of advantages such as low-temperature processing and the ability to prepare materials in various shapes, compared with the conventional preparation procedures of glass and ceramics. However, as-prepared films by the sol-gel method are usually amorphous, and a high temperature process over 300°C is required to form anatase nanocrystals. Therefore, it is difficult to form anatase nanocrystals on the substrates with poor heat resistance such as organic polymers.

EP-A-0 859 385 (in the name of Monsanto Company) discloses a method for manufacturing photovoltaic cells comprising polycrystalline oxides exhibiting semiconductor functionality. Particles of the polycrystalline metal oxide can be prepared by hydrolysis of the corresponding metal alkoxide followed by optional physical treatments such as growth and particle size control through digestion under hydrothermal conditions at temperatures in the range of from 150 to 250°C, followed by high temperature (200-500°C) sintering and grinding of the resulting sintered product to the required particle size. Said particles are then dye coated and suspended to yield a ink suspension, optionally containing additives, e.g. dispersants which can enhance the even distribution of the ink particles on the substrate where the ink suspension is deposited to yield a uniform layer. The so deposited layer is treated under mild and non-destructive conditions including temperatures below 180-150°C, possibly combined with non-destructive pressure e.g. below 20 bars, and/or evaporation under sub-atmospheric pressures. No specific examples are provided.

EP-A-1 167 296 (in the name of Kawasaki Jukogyo Kabushiki Kaisha) relates to a process for producing anatase titanium oxide having photocatalytic activity and large specific surface area. Anatase particles are prepared by a sol-gel method starting, for example, from a metal oxide or alkoxide heat treated in a closed vessel in the temperature range of 80 to 250°C. The examples show that a temperature of about 240°C is necessary to obtain the anatase phase while operating at atmospheric pressure.

EP-A-1 182 169 (in the name of Japan Science and Technology Corporation) relates to a process for producing anatase titania or composite oxide containing anatase titania wherein a gel containing a metal oxide is formed from a solution containing a hydrolysable titanium compound and an organic polymer (e.g. polyethylene glycol), and subsequently the gel is allowed to react with water at a temperature of 100°C or below.

Matsuda A. et al., J. Am. Ceram. Soc., **83** [1], 229-31, 2000 describe the preparation of transparent anatase nanocomposite films on various type of substrates, including organic polymers, using a sol-gel method at temperatures lower than 100°C under ambient pressure. The homogeneous dispersion of titania particles in the matrix and control of the porosity cannot easily be attained. In the preparation of titania porous films, the particles have a tendency to aggregate in the sol and the resultant films usually become opaque. A large surface area, high transmittance of ultraviolet (UV) light and durability for photocatalytic activity are required for the host matrix in which anatase nanoparticles are dispersed without aggregation. This document proposes silica gel as matrix candidate. It is remarked that the formation of anatase nanocrystals is hardly observed in pure titania and is a unique phenomenon to the silica-titania system.

The Applicant faced the problem of obtaining a process for preparing a photovoltaic device including at least one film of a semiconductive metal oxide with a major amount of photocatalytic crystalline phase, said phase being nanosized and with a controlled porosity, by operating under non-destructive conditions so that a film of said semiconductive metal oxide can be deposited on a variety of substrates.

Such a goal is attained by preparing a semiconductive metal oxide with a major amount of nanosized photocatalytic crystalline phase, depositing a film thereof in the presence of a hydrosoluble organic polymer and a hydrolysable organic derivative of said metal, under non-destructive conditions.

The present invention relates to a process for preparing a photovoltaic device including at least one film of at least one semiconductive

metal oxide with a major amount of a nanosized photocatalytic crystalline phase, said process comprising the steps of

a) obtaining a semiconductive metal oxide with a major amount of photocatalytic crystalline phase;

b) forming a suspension of the semiconductive metal oxide in an aqueous solution containing at least a hydrosoluble organic polymer and a hydrolysable organic derivative of said metal;

c) depositing the resulting suspension on a substrate to give a film;

d) treating said film at a temperature ranging between about 30°C and about 100°C in the presence of water.

Examples of photovoltaic devices obtainable by the method of the present invention are photovoltaic cells to be included in environmental sensor, e.g. gas sensors, remote power systems, electric systems for satellites, chip cards, e.g. smart cards, pocket calculators, watches.

In another aspect, the present invention relates to a process for preparing a film comprising at least one semiconductive metal oxide with a major amount of a nanosized photocatalytic crystalline phase, said process comprising the steps of

a) obtaining a semiconductive metal oxide with a major amount of photocatalytic crystalline phase;

b) forming a suspension of the semiconductive metal oxide in an aqueous solution containing at least a hydrosoluble organic polymer and a hydrolysable organic derivative of said metal;

c) depositing the resulting suspension on a substrate to give a film;

d) treating said film at a temperature ranging between about 30°C and about 100°C in the presence of water.

Examples of semiconductive metal oxides are oxides of titanium, zirconium, hafnium, strontium, zinc, indium, yttrium, lanthanum, vanadium, niobium, tantalum, chromium, molybdenum, tungsten. Preferred semicon-

ductive metal oxide is titanium oxide (hereinafter referred to as "titania") with a major amount of anatase phase.

For example, films provided with the method according to the invention comprises nanosized photocatalytic crystalline phase in a percentage higher than 70% by weight, more preferably higher than 90% by weight, even more preferably, higher than 95% by weight.

Step a) of the present method may be carried out according to known technique. For example, in the case of titania, the anatase phase may be obtained by treating a hydrolysable precursor with an anhydrous alcohol, for example absolute ethanol, isopropanol or isobutanol, and water, and heating the resulting slurry at temperature ranging between about 300°C and about 700°.

A hydrolysable precursor can be selected from alkoxides, chlorides and bromides. In the case of titania, examples are tetra-isopropoxy titanium, tetra-n-butoxy titanium, tetrakis(2-ethylhexyloxy)titanium, tetrastearyloxy titanium, and titanium tetrachloride.

Hydrosoluble organic polymer useful in the present invention can be polyvinylpyrrolidone, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, cellulose acetate, cellulose nitrate, hydroxypropylcellulose, polyvinyl alcohol, polyvinyl acetate, polyvinyl chloride. Preferably, the hydrosoluble organic polymer is polyethylene glycol. Preferred polyethylene glycol according to the invention has molecular weight ranging between 600 and 300,000, preferably between 3,000 and 10,000.

When a hydrosoluble organic polymer according to the invention contains hydroxy groups, the percentage by weight of monomeric units bearing such groups is preferably lower than about 90%, more preferably lower than about 80%.

The hydrolysable organic derivative of said metal may be an ester derivative optionally containing one or more group/s selected from hydroxy, alkoxy, carbonyl and carboxy. In the case of titanium, it can be selected from titanium diisopropoxide bisacetyl acetonate, titanium dibutoxide bis2,4-pentanedionate, titanium lactate, titanium methacrylate triisopropoxide,

titanium methacryloxyethylacetoacetate triisopropoxide, titanium oxide bispentanedionate, titanium oxide bistetramethylheptanedionate, titanium diisopropoxide bisethylacetoacetate, titanium diisopropoxide bistetramethyl-heptanedionate, titanium allylacetoacetatetriisopropoxide. Preferably the hydrolysable organic titanium derivative is titanium diisopropoxide bisacetyl acetonate (hereinafter referred to as TiACAC).

The aqueous solution of step b) preferably comprises a stabilizer.

The stabilizer can be an organic acid such as acetic acid, citric acid, propionic acid, butyrric acid, butylacetic acid, vinylacetic acid, ossalic acid, succinic acid, maleic acid, adipic acid, stearic acid, lactic acid. Preferably the stabilizer is acetic acid.

Preferably said aqueous solution shows a molar amount of stabilizer more than double with respect the hydrolysable organic derivative. More preferably the molar ratio hydrolysable organic derivative/stabilizer is of from about 1:4 to about 1:10.

The aqueous solution of step b) may be prepared from a first solution of hydrosoluble organic polymer and a second solution of a hydrolysable organic derivative of said metal. Preferably, said second solution has a molar ratio hydrolysable organic derivative/water of from about 1:1 to about 1:100. More preferably, said ratio is of from about 1:2 to about 1:20.

Preferably, step d) of the invention is performed at a temperature ranging between about 80°C and about 100°C. The time of the treatment of step d) can range between about 2 hours and about 5 hours. Preferably, said step d) is preceded by a drying step. Said drying step can be performed at a temperature of about 70°C-90°C.

The process of the present invention yields a photovoltaic devices including a semiconductive metal oxide with a major amount of nanosized photocatalytic crystalline phase, with porosity and thickness suitable for photocatalytic application on various kind of substrates. Due to the low temperature employed the film can be deposited on substrates with low thermal resistance, such as those based on organic polymers, too.

Examples of substrates with low thermal resistance are polyethyleneterephthalate (PET), polyethylene (PE) and polyvinylchloride (PVC).

The presence of said hydrolysable organic derivative improves interconnections among the nanoparticles and enhance the electron percolation within the film.

In particular, said nanosized photocatalytic crystalline phase has a particle size ranging between about 1 and about 20 nm, preferably ranging between about 5 and about 10 nm.

The film provided by the method of the invention shows a porosity of about 40-80%, preferably about 50-60%.

The present invention will be now further illustrated by means of the following examples and Figure 1 showing X-ray diffraction (XRD) patterns of a film prepared according to the invention and of a film prepared according to the prior art.

Example 1

Titanium isopropoxide (8 ml, 97%, Aldrich) was added under stirring to absolute ethanol (92 ml, Carlo Erba Reagenti). The solution was dropwise added, under vigorous stirring to a solution ethanol/distilled water (250 ml, 1:1 by weight). The resulting colloidal suspension was kept under stirring for 10 minutes.

Said suspension was heated at 100°C for 15 hours, then at 400°C per 2 hours to yield a powder containing more than 95% of anatase titania with a particle size of 5-10 nm, calculated from XRD line broadening measurements using Scherrer equation

$$K \bullet \ell / FWHM \bullet \cos q$$

wherein K is the shape factor of the average crystallite;

ℓ is the wavelength,

FWHM is the full width at half maximum of an individual peak , and

q is the peak position..

The obtained powder (1.5 g) was admixed to a solution A (3.5 g) composed by solution B (1.4 g) and solution C (2.1 g), solutions B and C having the following composition:

- Solution B: 0.42 g of PEG 6000) (Aldrich) and 0.98 g of deionized water;
- Solution C: Ti-ACAC (Aldrich)/acetic acid (CarloErba) /H_2O 1/6/8.

The resulting slurry was deposited, by doctor-blade, on a 1.13 mm thick 7.5x3 cm PET substrate (Eurotroniks S.r.l.) to give a 100 μm thick film. The film was treated at 90°C for 1 hour, then at 90°C for 3 hours in deionized water. The obtained film has the XRD (X-ray Diffraction) pattern of Figure 1, showing an anatase percentage higher than 95%.

SEM (Scanning Electron Microscope) analisys showed that tha film has a porosity of 60%.

Example 2

A film was prepared according to what taught in EP 1 182 169, example 2.

Detection by X-Ray Diffraction carried on the film before the heat treatment in water showed that said film is composed by amorphous titania and PEG. After heat treatment in water a formation of anatase titania particles with a size of about 10-30 nm was observed, but in an amount lower then 10%, as from the XRD pattern of Figure 1.